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Two-particle Approach to the Electronic Structure of Solids I: Scattering in the Presence of the Coulomb Interaction

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Based on an extension of Hubbard's treatment of the electronic structure of correlated electrons in matter we propose a methodology that incorporates the scattering off the Coulomb interaction through the determination of a two-particle propagator. The Green function equations of motion are then used to obtain single-particle Green functions and related properties such as densities of states. The solutions in two- and single-particle space are accomplished through applications of the coherent potential approximation. The formalism is illustrated by means of calculations for a single-band model system representing a linear arrangement of sites with nearest neighbor hopping and an one-site repulsion when two electrons of opposite spin occupy the same site in the lattice in the manner described by the so-called Hubbard Hamiltonian.

I. INTRODUCTION

The study of the electronic structure of matter can be viewed as comprising two distinct yet interrelated components: Spectra - the energy distribution of the electronic states in a material and energies, a crucial factor in determining ground-state properties, such as equilibrium volumes and structures, phase stability and evolution, magnetic behavior and a host of other physical properties. Corresponding to these two components are two also formally distinct but also interconnected formal frameworks: scattering theory and global self-consistency. Scattering theory, on the one hand, is directed towards the determination of the states of the electrons as they move under the influence of the external (local) fields of the nuclei (ions) in matter and their mutual interaction. Global self-consistency accounts for the structure of the Hilbert space defined by the system of interacting electrons and its effect in determining which states are available to the system. It follows that the application of scattering theory must be applied so as to account for the features of the Hilbert space defined by the entire system of interacting electrons in a material, thus taking into account both the effects of exchange (Fermi statistics) and correlation (Coulomb repulsion). Hence follow both the practical and formal interconnection of spectra and energies on the one hand, and of scattering theory and global self-consistency on the other.

The search for a theory that accommodates the requirement of a self-consistent treatment of scattering (in the sense just described) in the study of electronic structure has a long history, going back almost as far as the very inception of quantum mechanics. It is a search actively pursued to this day. It can be said that the modern formulation of the problem grew out of a paper by Hubbard[1] in 1963 in which he set out a formal procedure for the study of so-called strongly correlated electrons in matter focusing on the treatment of the scattering aspects of the problem. A year later, Hohenberg and Kohn[2] published their seminal paper on density functional theory (DFT) that can be viewed as the first attempt to account for both the scattering and self-consistent aspects of electronic structure within a unified formal framework. Density functional theory was developed quickly following that paper with a number of works[3-5] - much too numerous to attempt anything but a cursory review here - codifying its implementation within the so-called local density approximation (LDA)[6-8] for the case of ordered, elemental solids[9] and ultimately alloys characterized by chemical disorder[10, 11].

The success enjoyed by the LDA in providing deep insight in tracing the electronic basis of materials behavior can hardly be overstated. At the same time, it is well known that the LDA can fail to give an accurate picture of physical properties, such as spectra, and also energetics for a number of systems, especially ones in which correlation effects are judged to play a prominent role. It is generally acknowledged that the shortcomings of the LDA derive from its particular treatment of correlation effects. Consequently, a number of methodologies have been put forward[12-17] - again space constraints preclude all but a short listing of such methods - directed at ameliorating one or another of the disadvantages of the LDA. Most recent developments include the introduction and implementation of dynamical mean field theory DMFT[18] and the coupling of that theory with the LDA[19], and self-consistent extensions[20, 21] of the GW approximation. In spite of this great effort, however, the development of a unique formal framework that accounts for both the scattering aspects and the global self-consistency requirement of the problem, and thus treating spectra and energies within a unified formalism has remained illusive. One difficulty is the possible overcounting of correlation effects when the Coulomb interaction is treated explicitly[14, 19] based on single-particle quantities, such as wave-functions determined within the LDA and consequently contain an accounting of correlation effects.

The present work is a contribution to the study of electronic structure of matter presenting the first phase of a methodology developed to satisfy the requirement of global self-consistency when treating the scattering aspects of the problem. It is based on the formal concepts presented by Hubbard[1] although it departs from Hubbard's treatment by providing for the determination of a two-particle propagator describing scattering off the mutual interaction of two particles. Thus, the scattering aspects of electronic structure are developed explicitly in the rest of the manuscript. Also, it allows the treatment of both electrons and holes (absence of an electron) on an equal footing when determining spectral properties. How the self-consistent part of electronic structure is to be taken into account is commented upon, but will be presented in detail in a future publication.

The formalism proposed here is based on the calculation of propagators in two-particle space from which a single-particle Green function can be obtained through a solution of the equations of motion of many-body theory[22–24]. The calculation of such propagators allows the treatment of the scattering caused by the Coulomb repulsion within the context of canonical scattering theory, namely as the scattering of a wave by a field that is confined to the space of wave propagation (external field). Thus, the Coulomb interaction is treated on a par with the scattering off the potentials associated with the presence of ionic charges in a material. Further features resulting from the study of two-particle Green functions will be discussed in connection with the treatment of the self-consistent aspects of electronic structure to be presented in future work.

The computational aspects of the problem proceed along the following lines. First, a *two-particle propagator* is determined describing the propagation of a *single particle* (either electron or hole) as it proceeds under the influence of both ionic potentials and the Coulomb interaction with another particle (of opposite spin). Because the scattering off the Coulomb potential depends on whether a particle encounters another particle or not on a given site of the material, the problem is fundamentally one of disorder scattering, both at the two-particle and the single-particle level. It can be addressed at both levels by implementing appropriate extensions of the coherent-potential approximation (CPA)[10, 25–27], leading to a single-particle self-energy (here considered to be site-diagonal) that is complex and energy dependent, and can be easily seen to possess the proper mathematical structure in the complex energy plane.

The developments presented below are based on the so-called Hubbard Hamiltonian (see following section). The consideration of *ab initio* implementation will be taken up in a paper currently under consideration.

II. REVIEW OF HUBBARD'S WORK

The by now traditional Hubbard Hamiltonian can be written in the so-called tight-binding form,

$$H = \sum_{i,\sigma} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} + \sum_{i \neq j, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\sigma} n_{i\bar{\sigma}}. \quad (1)$$

Here, the operators $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) describe the creation (annihilation) of an electron of spin σ at site i , ϵ_i denotes the on-site potential (site energy) at i , the quantities t_{ij} describe electron propagation between sites i and j , and U denotes the Coulomb repulsion acting on two electrons of opposite spin when found on the same site. The symbol $\bar{\sigma}$ denotes a spin opposite to σ . We consider the Hamiltonian in the last expression for the case of a single-band Spin-compensated system (maximum occupancy two electrons per site and equal numbers of electrons of either spin.) We denote the number of electrons per site, the so-called band-filling, by n . Then $n/2$ denotes the number of electrons of a given spin per site in the material.

One property of the Hamiltonian in the last equation must be kept in mind: it describes an inherently fluctuating system because (away from the limits of a completely empty or completely full band) an electron can encounter either another electron or a hole on site i , leading to scattering resonances whose strength and weight depend directly on the number of electrons per site. In the following, this disorder-like aspect of the problem is handled through the use of the CPA formalism, applied to both the propagation of waves in single-particle space and in two-particle space.

An expression for the Green function, $G_{ij}^\sigma(z)$, for a particle of spin σ at complex energy z can be obtained based on the commutation relations of the Hamiltonian of Eq. (1) with various operators. From the relations[1],

$$[c_{i\sigma}, H] = \epsilon_i c_{i\sigma} + \sum_{i'j} t_{ij} c_{j\sigma} + U c_{i\bar{\sigma}}^\dagger c_{i\bar{\sigma}} c_{i\sigma} \quad (2)$$

and

$$[n_{i\sigma}, H] = \sum_{i'j} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} - c_{j\sigma}^\dagger c_{i\sigma}), \quad (3)$$

we obtain

$$(z - \epsilon_i)G_{ij}^\sigma(z) = \delta_{ij} + \sum_{i \neq k} t_{ik} G_{kj}^\sigma(z) + U \Gamma_{ii;j}^{\sigma\bar{\sigma}}, \quad (4)$$

where the quantity $\Gamma_{ii;j}^{\sigma\bar{\sigma}}$ describes the motion of a single electron in two-particle space and itself satisfies the equation of motion,

$$\begin{aligned} (z - \epsilon_i) \Gamma_{ii;j}^{\sigma\bar{\sigma}} &= \langle n_{i\bar{\sigma}} \rangle \delta_{ij} + U \Gamma_{ii;j}^{\sigma\bar{\sigma}} \\ &+ \sum_{k \neq i} t_{ik} \Gamma_{ik;j}^{\sigma\bar{\sigma}} + \sum_{k \neq i} t_{ik} [\Gamma_{ii;kj}^{\sigma\bar{\sigma}} - \Gamma_{ki;jj}^{\sigma\bar{\sigma}}]. \end{aligned} \quad (5)$$

The last expression bears scrutiny. The quantity $\Gamma_{ii;j}^{\sigma\bar{\sigma}}$ is denoted by Γ_{ij}^σ by Hubbard[1] and is defined as the Green function $\langle\langle c_{i\bar{\sigma}}^\dagger c_{i\bar{\sigma}} c_{i\sigma}; c_{j\sigma}^\dagger \rangle\rangle$ (for details, see the original paper by Hubbard.) Its equation of motion involves the more general elements $\langle\langle c_{i\bar{\sigma}}^\dagger c_{l\bar{\sigma}} c_{k\sigma}; c_{j\sigma}^\dagger \rangle\rangle$ of the two-particle propagator that is denoted by $\Gamma_{ik;l,j}^{\sigma\bar{\sigma}}$ in the notation used in the expressions above. As pointed out by Hubbard, the on-site nature of the Coulomb repulsion in the Hamiltonian (1) leads to a closed form of the equation of motion for Γ . In Hubbard's treatment, matrix elements other than $\Gamma_{ii;j}$ were approximated by terms proportional to the single-particle Green function, G_{ij} . In what follows, we pursue a solution for the matrix Γ and obtain the single-particle Green function form Eq. (4).

Note the similarity in the structure of the terms involving electron hopping in Eqs.(3) and (5). In the former, they describe the hopping of an electron, spin σ , between two different sites. In the latter, they describe the hopping of an electron of spin σ , the electron whose motion is explicitly being studied by these equations, between sites i and k while an electron of opposite spin remains on site i . The last term in Eq. (5) describes the propagation of an electron of spin $\bar{\sigma}$, (the "other" electron), between sites i and k while the electron of spin σ , the one whose motion is described by G_{ij}^σ propagates between sites i and j .

The last expression shows that the equation of motion for the propagator Γ forms a closed expression in the space of two particles, and can be solved by matrix inversion in that space. The corresponding matrices take the following form:

Let R_i be the physical space defined by electron i , $i = 1, 2$, and let $I_{(i)}$ denote the identity operator in that space. Let also $H_{(i)}$ denote a Hubbard-like Hamiltonian, Eq. (1), for electron i , and let $T_{(i)}$ denote the kinetic energy operator (whose matrix elements are given by the t_{ij}) for electron i . The Hamiltonian describing the motion of a single electron in the space of two particles in the absence of inter-particle interactions is now given by the expression,

$$H_{(1,2)}^0 = H_1 \otimes I_{(2)} + T_{(2)} \otimes I_{(1)}, \quad (6)$$

where the superscript 0 denotes the vanishing of the interaction U , and the subscript (1, 2) denotes a Hamiltonian in two-particle space. With U set equal to 0, the matrix elements of the quantity

$$\Gamma^0(z) = [z - H_{(1,2)}^0]^{-1}, \quad (7)$$

are obtained directly from Eq. (5) (with $U = 0$.)

The space of $H_{(1,2)}$ is the tensor product $R_1 \otimes R_2$. Each site in this space signifies a possible encounter of two electrons of opposite spin giving rise to a potential U , the chance of such an encounter depending on band filling. Because of this, U can be viewed as a site-diagonal, external random field in the space of Γ . With this in mind, we can write,

$$\Gamma(z) = [z - H_{(1,2)}^0 + U]^{-1}, \quad (8)$$

for the matrix representing the motion of an electron in two-particle space in the presence of the interaction U .

The chance of encountering a scattering potential U on a site depends on band filling (average number of electrons per site), n . For example, a filled band (in a single-band system) corresponds to $n = 2$, and a half-filled band to $n = 1$. Correspondingly, the number of electrons of a given spin per site equals $n/2 = 1$ and $n/2 = 0.5$ in these two cases.

A simple example may serve as illustration of the points made above. In the so-called atomic limit, (vanishing t_{ij}), and considering that the on-site energies ϵ_i are independent of site index, one finds[1],

$$G_{ij}^\sigma(z) = \delta_{ij} \left\{ \frac{1 - n/2}{z - \epsilon} + \frac{n/2}{z - \epsilon - U} \right\}. \quad (9)$$

We are now ready to consider the treatment of the general case of non-vanishing interaction and away from the atomic limit. This can be done most conveniently by rewriting the last expression, and re-interpreting the resulting form.

A. Particles and holes

The last equation gives the spectrum of the single-particle propagator as consisting of two parts centered at resonances at energies ϵ and $\epsilon + U$. The resonance at ϵ corresponds to the non-interacting part of the system while that at $\epsilon + U$ to the interacting part. The equation can be recast so as to describe the occupied and unoccupied parts of the spectrum (respectively ground and excited states) and yield a symmetric description of both electrons and holes.

Shifting the zero of energy to $U/2$, we can write the last equation in the form,

$$G_{ij}^{\sigma}(z) = \delta_{ij} \left\{ \frac{1 - n/2}{z - \epsilon + U/2} + \frac{n/2}{z - \epsilon - U/2} \right\}. \quad (10)$$

We can now interpret the resonance at the lower energy $-U/2$ as corresponding to the occupied (ground) states in the system, while that at the higher energy $U/2$ corresponds to the excited states. In this interpretation, a particle can signify either a hole (at the lower part of the spectrum) or an electron (at the upper part). In other words, the ground state is the part of the spectrum in which states are filled and thus *holes can be created* through the removal of an electron. Correspondingly, the excited states are empty so that an *electron can be created* there. We name the parts of the spectrum according to the kind of particle that can be created, so that the ground state corresponds to holes and the excited states to electrons.

The most significant part of the interpretation just given is that the notion of a single particle encompasses both electrons and holes, and can be used to provide an equivalent description of electron and hole propagation in the system. We can think of the distinction as being associated with the scattering potential encountered by a *single-particle wave* as it propagates through single-particle space (here in the atomic limit.) The wave scatters off $-U/2$, and yields a sub-band associated with the ground (hole) states, or can scatter off $U/2$ yielding a sub-band corresponding to the excited states. It is easily seen that this description satisfies all limiting requirements, yielding exact expressions in the non-interacting and atomic limits.

The language used in the previous paragraph can be connected to the discussion of electrons in a substitutionally disordered alloy, described, for example, by a Hamiltonian of the tight-binding kind. In the alloy case, a wave representing an electron propagates through a medium characterized by the presence of potentials whose strength varies from site to site according to some statistical distribution. A disordered binary alloy A_cB_{1-c} , for instance, can be modeled as a random distribution of scattering potentials (on-site energies), ϵ_A and ϵ_B over the sites of a lattice with corresponding probabilities c and $1 - c$.

Similarly, a single-particle wave can be considered as propagating in a space characterized by potentials whose strength and weight vary according to the energy region and band filling (that now plays the role of concentration). Although the physical content of the alloy description is quite different from that of the description of electron and holes in an interacting system, the formal similarity between the equations used in these descriptions allows the use of methodology employed in the study of alloys to the case of interacting electrons and holes. The practical ramifications of this statement are set forth in the following section.

III. THE CPA IN TWO- AND SINGLE-PARTICLE SPACES

The coherent potential approximation (CPA)[10, 11, 25, 26] is well known in the study of alloy physics. It represents arguably the most satisfactory approximation scheme for the study of disorder, in terms of its analytic properties, satisfaction of various sum rules and its behavior in various physical limits. The formal aspects of the method are the subject of innumerable writings and are well known. It suffices to say that the method is applicable to alloys of an arbitrary number of constituent species where it yields sub-bands associated with each one of these species. It is this particular feature that is exploited in using the CPA to study wave propagation (particle propagation) through a system described in terms of electron and hole scattering.

A. Coherent Potential Approximation

The scattering off particle configurations is statistical in nature requiring a treatment of a wave scattered by a random field. This treatment can be provided by means of the coherent potential approximation[25, 26] both in two-particle as well as in single-particle space. In both applications, the analogy to the case of ordinary alloys plays an instructive role.

A single-particle wave (in single-particle space) propagates from site to site being scattered there by the potential corresponding to the occupation of the site by either electrons and/or holes. That potential fluctuates because the

occupancy of a site changes as electrons hop on or off. Our aim is to approximate the scattering off the various sites by means of an effective field obtained through the CPA.

The CPA self-consistency condition in single-particle space requires the study of two-particle propagators, as described in Eq. (4) and (5). Correspondingly, a solution for Γ is to be obtained through the CPA in two-particle space.

B. CPA in two-particle space

A wave described by the propagator of Eq. (8) scatters off the possible configurations of a site in the lattice that now appear as local external fields. In this description, all sites in the space of propagation of Γ are equivalent, thus yielding a medium that is translationally invariant, each providing a random scattering field: When the site is occupied by two holes, it is assigned a scattering strength of $-U/2$ with a weight (probability or concentration) of $(1 - n/2)^2$. Similarly, a configuration containing an electron and a hole provides scattering at energy 0, with a weight of $2(1 - n/2)n/2$, while the presence of two electrons provides a scattering strength of $U/2$ with weight $(n/2)^2$. The use of the CPA condition[25, 26] applied to a ternary alloy yields an effective medium of propagation characterized in two-particle space by a site-diagonal self-energy, $\Sigma^{(2)}$, and gives three components of the quantity Γ : $\Gamma(-U/2)$, $\Gamma(0)$ and $\Gamma(U/2)$.

Letting α denote the various scattering strengths, and n_α the corresponding weights (probabilities) the self-consistent equation determining an effective two-particle propagator is expressed in terms of the site-diagonal elements of Γ and takes the form,

$$\bar{\Gamma}_{00;00}(z) = \sum_{\alpha} n_{\alpha} \Gamma_{00;00}^{\alpha}(z). \quad (11)$$

Here, the individual components $\Gamma_{00;00}^{\alpha}$ take the form,

$$\Gamma_{00;00}^{\alpha}(z) = [z - \alpha - \Delta^{(2)}]^{-1} \quad (12)$$

where the so-called renormalized interactor[27], $\Delta^{(2)}$, describes the interaction of a site in two-particle space with the surrounding medium that is in turn characterized by a self-energy, $\Sigma^{(2)}$. The approach to the self-consistent solution of the CPA equations is based on the site-diagonal element of the two-particle effective medium propagator written in terms of the corresponding self-energy,

$$\bar{\Gamma}_{00;00} = \int d\mathbf{k} d\mathbf{q} [z - \Sigma^{(2)} - S(\mathbf{k}) - S(\mathbf{q})]^{-1}, \quad (13)$$

where the structure factors $S(\mathbf{k})$ and $S(\mathbf{q})$ are the structure factors (Fourier transforms of the hopping terms) for each of the individual single-particle spaces forming two-particle space. (In the case of single-band systems, such as those discussed in the section of numerical applications, the last expression involves strictly scalar quantities and is correct as it stands. For the case of systems characterized by multiple bands, the structure factors must be properly rotated vertically with respect to one another using the appropriate rotation transformations in two-particle space.)

The determination of $\bar{\Gamma}$ and of the various Γ^{α} allows the use of the equation of motions, Eq. (4) and (5) in determining the single-particle Green function.

C. Single-particle Green functions

The site-diagonal elements of the single-particle Green function can now be determined through Eq. (4) applied to the components $\Gamma_{00;00}(-U/2)$ and $\Gamma_{00;00}(U/2)$ (there is no direct coupling to the scattering at zero energy.) This gives two components for the single-particle propagator (with all indices suppressed),

$$G(\pm U/2) = G^0[1 + (\pm U/2)\Gamma(\pm U/2)], \quad (14)$$

where G^0 denotes the single-particle propagator in the absence of the interaction.

The site-diagonal part of the single-particle Green function describing both the electron and hole parts of the spectrum is now given by an average over band filling (CPA averaging),

$$\bar{G}_{ii} = (1 - n/2)G_{ii}(-U/2) + (n/2)G_{ii}(U/2). \quad (15)$$

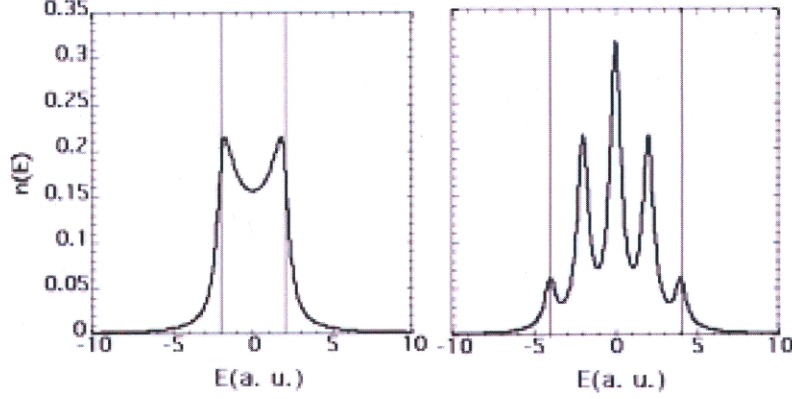


FIG. 1: Non-interacting densities of states in single-particle (left panel) and two-particle space (right panel) for a single-band system on a linear chain with nearest neighbor hopping. The DOS in two-particle space corresponds to a finite square of 16 sites with periodic boundary conditions. The vertical lines denote the edges of the bands in single-particle (left panel) and two-particle space (right panel), respectively.

This is the CPA equation corresponding to a two-component alloy with a fundamental difference from the form that it takes in the case of ordinary alloys. Now, the calculation of the single-particle Green function corresponding to each subspecies (scattering by holes or electrons) is to be determined throughout the prior calculation of a propagator in two-particle space.

It is easily shown that the matrix elements G_{ii} corresponding to scattering by an electron or a hole can be written in the form,

$$G(\pm U/2) = [z - \Delta - (\pm U/2) \frac{z - \Delta}{z - \Delta^{(2)}}]^{-1} \quad (16)$$

where the quantity Δ is the renormalized interactor in single-particle space. This expression makes clear the manner in which the interparticle interaction couples the single-particle and two-particle spaces.

As in the case of the ordinary CPA for disordered alloys, a site-diagonal self-energy $\Sigma^{(1)}$ can now be calculated by noting that the site-diagonal elements of the effective single-particle Green function can be obtained as an integral,

$$\bar{G}_{ii}(z) = \int d\mathbf{k} [z - \Sigma^{(1)} - S(\mathbf{k})]^{-1}, \quad (17)$$

which can also be written in the form,

$$\bar{G}_{ii}(z) = [z - \Sigma^{(1)} - \Delta]^{-1}. \quad (18)$$

These equations can be iterated to yield a single-particle self-energy $\Sigma^{(1)}$. The equation to be iterated for $\Sigma^{(1)}$ can be written in the form,

$$\Sigma^{(1)} = z - \Delta[\Sigma^{(1)}] - \bar{G}^{-1}. \quad (19)$$

The results of numerical applications of these equations are reported in the following section.

IV. NUMERICAL RESULTS

The formal considerations presented in previous sections have been applied to model systems corresponding to a linear chain with nearest neighbor hopping, set equal to one in arbitrary units, $t = 1$, described by the single-band Hamiltonian shown in Eq. (1). The site energies are set equal to zero throughout.

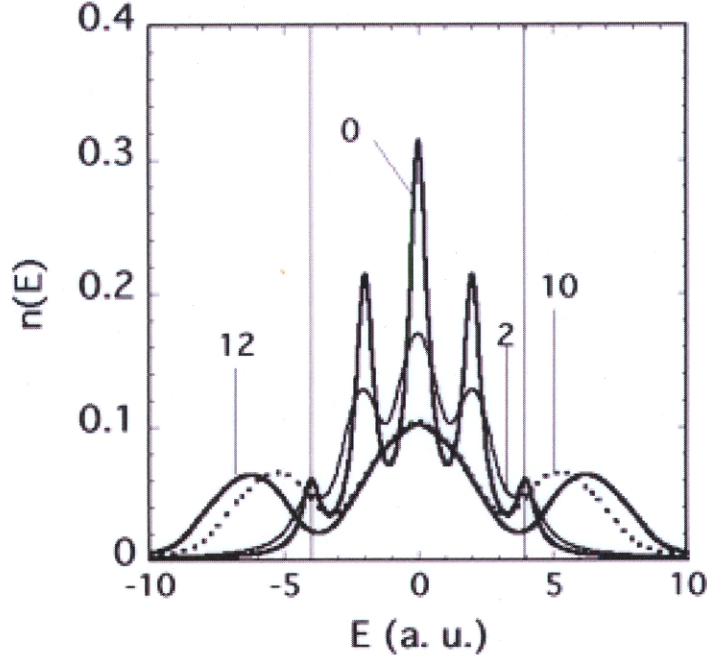


FIG. 2: Densities of states in two-particle space (4x4 square) for various values of the interaction as indicated.

The left panel of Fig. (1) shows the single-particle density of states (DOS) vs. energy for a single-band model system on linear chain with nearest neighbor hopping (set equal to one) in the absence of the interaction, $U = 0$. It is well known[28] that the DOS for such a system are given by the expression,

$$n(E) = \Im \frac{1}{\sqrt{z^2 - 4t^2}}, \quad (20)$$

and exhibit inverse square root singularities at the band edges, $\pm 2t = \pm 2$ (as indicated by the thin vertical lines).

In all calculations a small imaginary part was assigned to the energy so as to enhance convergence of the self-consistent equations. Because of this, the singularities at the band edges are smoothed over and the DOS exhibits tails that decay exponentially into the regions below and above the band edges.

The two-particle space corresponding to the infinite linear chain with nearest neighbor hopping is an infinite square with nearest neighbor hopping. For ease of calculation, the infinite square has been approximated by a square of finite size, with four sites on a side and periodic boundary conditions. Total DOSs in two-particle space are determined from the imaginary part of the site-diagonal elements $\bar{\Gamma}_{00;00}$. The spectra corresponding the finite, 16-side square at $U = 0$ are shown in right panel of Fig. (1). We note that the edges of the band occur at $\pm 4t = \pm 4$, and the spectra are thus twice as wide as those of the single-particle case shown in the panel on the left. Again, sharp features in the DOS have been smoothed over because of the assignment of a small imaginary part to the energy.

In the case of a finite interaction, the structure develops into three sub-bands, one for each of the scattering strengths, $-U/2$, 0 and $U/2$, whose weights, in the case of half-filling are $1/4$, $1/2$ and $1/4$, respectively. As indicated in Fig. (2) these sub-band are clearly separated for large enough values of U , each having essentially the same overall shape as the non-interacting band in right panel of Fig. (1), but with disorder smoothing over the structure of the bands with increasing U .

Figure (3) shows the evolution of the single-particle DOS with increasing value of the on-site interaction U at half filling, $n/2 = 0.5$. In this case, the Fermi level is at $E = 0.0$.

We note that increasing U causes the appearance of side bands above and below the central structure whose weight diminishes as these sub-bands are pulled further and further apart. For large enough values of the interaction, two

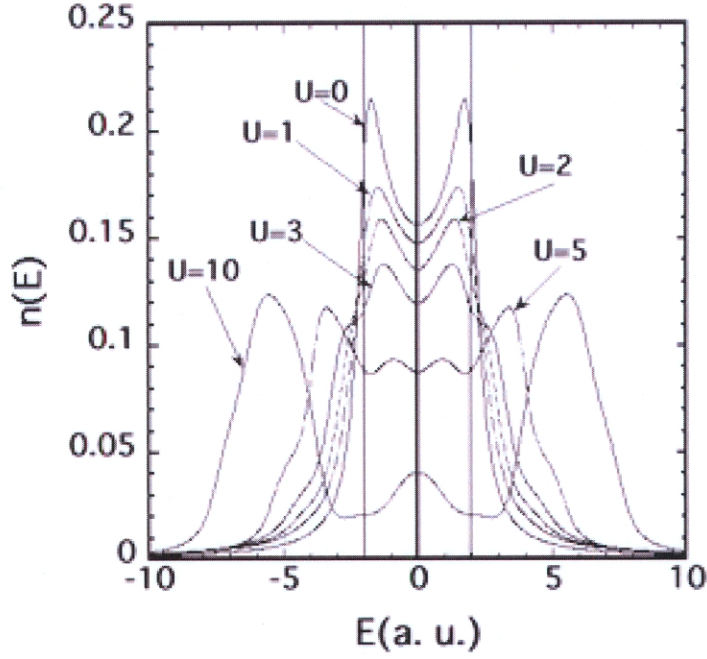


FIG. 3: Densities of states in single-particle space for a half-filled single band model system on a linear chain with nearest-neighbor hopping and for various values of the interaction as indicated.

well-formed sub-bands appear, symmetrically arranged about the center of the gap region between them. These are the well-known Hubbard sub-bands whose structure bears close scrutiny.

First, it is noted that the bands are somewhat wider than the DOS for the non-interacting case, left panel in Fig. (1), their width approaching that of the two-particle spectra, right panel in Fig. (1). We also note the general structure of the sub-bands reflecting that of the two-particle DOS, right panel in Fig. (1). These features arise because of the direct dependence of the single-particle Green function on the two-particle propagator, as exhibited in the equations of motion. This dependence causes the gap to form when the strength of the interaction essentially exceeds the width of the two-particle spectrum (although the effective width of the single-particle sub-bands is somewhat smaller than that of the two-particle DOS.)

Also, we note the central peak (at $E = 0$) that persists even when the gap is fully formed. Its presence can be traced to a scattering resonance at $E = 0$ in two-particle space. Even though the single-particle Green function does not couple directly to that scattering mode, the modes that it does couple to, namely $\pm U/2$, carry information about the scattering at $E = 0$.

This resonance corresponds to the so-called quasi-particle peak observed in photoemission spectra near the Fermi level in strongly correlated systems, and interpreted to correspond to a quasi-particle at zero energy. This peak should disappear once the gap is formed, although it persists in the results exhibited here. This behavior can be understood along the following lines.

In an exact treatment of a correlated system (such as the one treated here), configurations associated with scattering strengths $\pm U/2$ are directly coupled to one another through the hopping of a single particle (electron or hole) from site to site. Thus they form sub-bands whose structure reflects that of the non-interacting system. Scattering resonances at $E = 0$ do not couple to one another especially in the case of a half-filled band. The hopping of electrons or holes in one such configuration cannot lead to another at the same scattering resonance but must proceed through coupling to the resonances at $\pm U/2$. In this sense, the resonances at $E = 0$ act in the manner of isolated impurities in a host material, their width arising through hybridization with resonances near them in energy.

For sufficiently small values of U , this hybridization has enough strength to provide an observable width to the

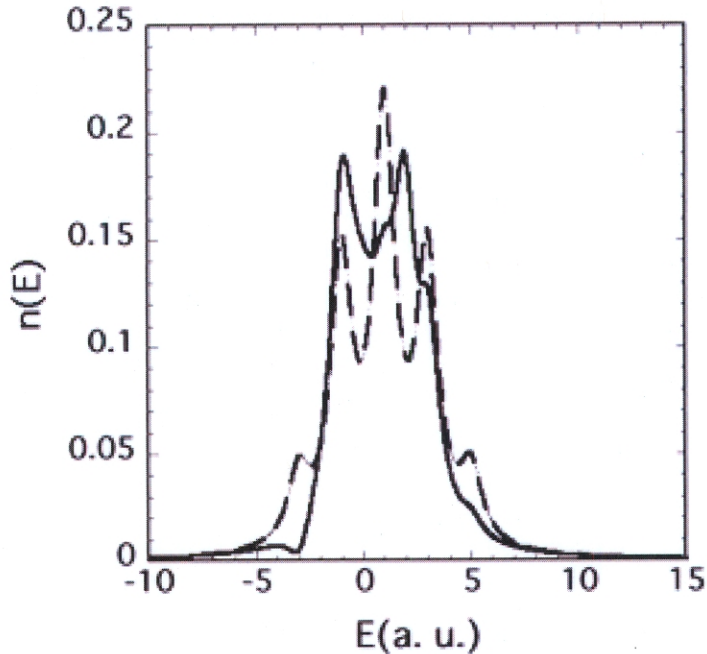


FIG. 4: Densities of states in single-particle space (solid curve) and for two-particle space, represented here by a 4×4 square (dashed curve), for a nearly empty single band model system on a linear chain with nearest-neighbor hopping and for $U = 2.0$.

resonance at $E = 0$. As U increases (essentially moving outside the spectrum of two-particle states), hybridization decreases rapidly with the ultimate effect the disappearance of the resonance once the gap is formed.

This exact behavior cannot be reproduced exactly within the CPA formalism used here for two reasons: First, the present application does not distinguish between resonances coupled to one another from the isolated ones that do not. Also, the finite imaginary part assigned to the energy provides an effective hybridization that persists even when the gap is fully formed.

Finally Figs. (4) and (5) exhibit single-particle spectra for the case of nearly empty band, $n/2 = 0.01$, and for two values of the inter-particle interaction $|\pm U/2| = 2$ and $|\pm U/2| = 5$. It is seen that now the spectrum lies almost exclusively in the unoccupied part, as expected. Also, for the smaller value of the interaction, it is essentially identical to that of the non-interacting spectrum, while it approaches closely that of the two-particle spectrum at the larger value, $U/2 = 10$.

In the case of a half-filled band, the Fermi level lies at $E = 0$. In cases deviating from that of half filling, the Fermi level is to be determined by integrating over the spectra until the value of the integral reaches the pre-assigned value of n .

V. GLOBAL SELF-CONSISTENCY

The formalism in the previous section was directed at the calculation of spectra (DOSs) in the presence of the Coulomb repulsion described within the Hamiltonian of Eq. (1). It was shown that the calculation proceeds in two steps, both based on the application of the CPA, first in two-particle space and subsequently in single-particle space relying on the results of the prior calculation. This procedure provides a self-energy that reflects only fluctuations at the level of two particles (and ultimately a single particle) and does not take into account the presence of the remaining particles in the system.

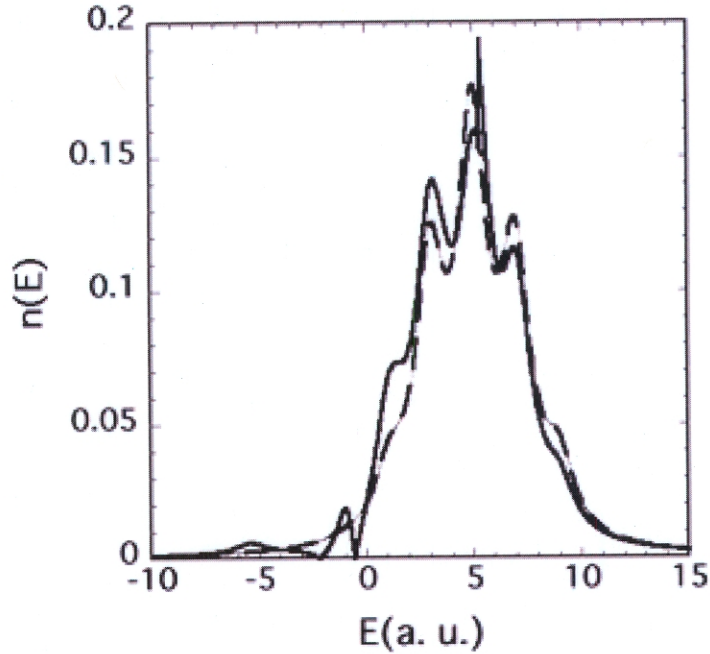


FIG. 5: Results analogous to those of the previous figure but for $U = 10.0$.

Global self-consistency refers to a procedure that would allow the study of scattering processes in matter in a way that captures the structure of the Hilbert space determined by the system as a whole. Density functional theory (within its LDA implementation) provides for such self-consistency within the level of a single-particle. DFT can be viewed as a prescription for embedding a single electron (the space of a single particle) in a medium that acts on the particle by means of an appropriately defined, albeit approximate, potential. This is the potential obtained in LDA calculations that includes the Coulomb interaction between a single particle and all other particles in the system, and also the exchange correlation potential.

Treatments based on the traditional form of DFT/LDA (within single-particle space), however, suffer from the limitation arising when the scattering off the Coulomb interaction, a potential fully defined only within two-particle space, is approximated by means of scattering off a real potential confined to the space of a single particle. Thus, they are likely to miss-represent both the position and the shape of the resonances arising because of the scattering by the Coulomb field.

It has been suggested[29–31] that the formal framework of DFT be extended to two-particle densities in order to account for the Hilbert space in the study of scattering in two-particle space. One could expect that such a treatment might improve both the position and the shape of scattering resonances leading to a more accurate determination of spectra than is afforded by current applications. Through the determination of a density in two-particle space, it would also remove the difficulties associated with the so-called self-interaction problem that arises in current implementations of DFT/LDA. The generalization of DFT/LDA may also be useful in providing an effective termination of the Green function equations of motion that would emerge in a treatment in which the Coulomb repulsion is assigned its full range rather than being restricted to an on-site form.

The practical application of two-particle DFT hinges crucially on the determination of a corresponding exchange-correlation potential, and work aimed at the determination of such a potential is currently underway.

VI. DISCUSSION AND CONCLUSION

The calculation of electronic structure of matter hinges on describing the effect on the electron gas produced by the fields set up by ionic charges in a material and the mutual interaction among the electrons (Coulomb interaction). This description is to be carried out in a way that captures the structure of the Hilbert space defined by the entire system of electrons and nuclei.

One obstacle in obtaining an accurate description of the scattering aspects of the problem (even in the absence of self-consistency) is the study of the scattering off the Coulomb potential carried out by means of a real potential confined to single-particle space. The formalism presented in this paper provides for a treatment of the scattering off the mutual interaction between two particles within a two-particle space in which this interaction appears as a local external field. It is thus amenable to treatment by means of ordinary scattering theory.

The approach developed above is based on the formalism originally developed by Hubbard[1] but extends that formal approach to incorporate the solution of a two-particle propagator directly, and subsequently obtain the single-particle Green function by means of the Green function equations of motion. The resulting methodology allows a fairly straightforward interpretation and explanation of a number of features, such as the position and shape of the spectra, of the DOS associated with an interacting electron system. It also allows the equivalent treatment of particles and holes in the system, and the determination of the relative weights of occupied and excited states depending on bandfilling (number of electrons per site).

It remains for future work to provide the incorporation of the ideas presented here into a globally self-consistent methodology that would account for the presence of all electrons in the system.

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